U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-292 531

Anodic Stripping Voltammetry at a Mercury Film Electrode: Baseline Concentrations of Cadmium, Lead, and Copper in Selected Natural Waters

(U.S.) Environmental Research Lab.-Duluth, MN

30 Jan 78

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completi

1. REPORT NO.	2.	3. PB 292531
EPA-600/J-78-088	JOURNAL ARTICLE	

4. TITLE AND SUBTITLE	5. REPORT DATE
Anodic Stripping Voltammetry at a Mercury Film Electrode: Baseline Concentrations of Cadmium, Lead, and Copper in Selected Natural Waters	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J. E. Poldoski and G. E. Glass	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Environmental Research Laboratory-Duluth 6201 Congdon Boulevard Duluth, Minnesota 55804	10. PROGRAM ELEMENT NO. 1BA608
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Same as above	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA-600/03

15. SUPPLEMENTARY NOTES REFERENCE: Poldoski, J.E., and G.E. Glass. 1978. Anodic Stripping Voltammetry at a Mercury Film Electrode: Baseline Concentrations of Cadmium, Lead, and Copper in Selected Natural Waters. Analytica Chimica Acta 101: 79-88.

16. ABSTRACT

A simple, rapid, and inexpensive anodic stripping voltammetric method with a mercury thin film electrode is reported for the establishment of baseline concentrations of cadmium, lead, and copper in natural waters. The procedure for routine surface preparation of wax-impregnated graphite mercury film electrodes requires about 30 min. Concentrations in the 0.006-6 $\mu g/l^{-1}$ range are determined by linear d.c. voltage sweeps; the total time for a plating and stripping cycle is 6 min or less. The need for pressure-digesting samples for copper determinations is demonstrated. The a.s.v. results correlate well with corresponding analyses performed by graphite-furnace atomic absorption spectrometry.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Electrode Trace analysis Voltammetry Cadmium Lead Copper Water	Anodic stripping voltammetry Trace element analysis Water analysis Cadmium analysis Copper analysis Lead analysis Mercury film electrode	07B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	12
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	A02 - A01

REPRODUCED BY NATIONAL TECHNICAL INFORMATION SERVICE U.S. DEPARTMENT OF COMMERCE SPRINGFIELD, VA. 22161

EPA-600/J-78-088
JOURNAL ARTICLE

Analytica Chimica Acta, 101 (1978) 79—88
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

ANODIC STRIPPING VOLTAMMETRY AT A MERCURY FILM ELECTRODE: BASELINE CONCENTRATIONS OF CADMIUM, LEAD, AND COPPER IN SELECTED NATURAL WATERS

J. E. POLDOSKI* and G. E. GLASS

U.S. Environmental Protection Agency, Environmental Research Laboratory-Duluth, 6201 Congdon Boulevard, Duluth, Minnesota 55804 (U.S.A.)

(Received 30th January 1978)

SUMMARY

A simple, rapid, and inexpensive anodic stripping voltammetric method with a mercury thin film electrode is reported for the establishment of baseline concentrations of cadmium, lead, and copper in natural waters. The procedure for routine surface preparation of wax-impregnated graphite mercury film electrodes requires about 30 min. Concentrations in the 0.006—6 $\mu g\ l^{-1}$ range are determined by linear d.c. voltage sweeps; the total time for a plating and stripping cycle is 6 min or less. The need for pressure-digesting samples for copper determinations is demonstrated. The a.s.v. results correlate well with corresponding analyses performed by graphite-furnace atomic absorption spectrometry.

Characterizing trace elements in aquatic environments has become increasingly important, especially with reference to natural or relatively unpolluted conditions, such as those generally found in Lake Superior [1]. However, few analytical procedures are capable of measuring these characteristically low concentrations, and those which can are sometimes cumbersome and require a sample preconcentration step. Cadmium, lead, and copper are heavy metals which are often of concern because of their high toxicity, especially to aquatic life [2—5]. Fortunately, these three metals are amenable to determination by several electrochemical techniques, particularly anodic stripping voltammetry (a.s.v.). Although there are many published methods [6—13], few deal specifically with the accuracy attainable for these elements in waters where concentrations are very low. The objective of this paper is to describe the utility of a simple and inexpensive a.s.v. method and to explore various aspects of trace analyses for copper, lead, and cadmium in some natural waters.

EXPERIMENTAL

Electrode construction and preparation

The working electrode was a wax-impregnated graphite mercury film electrode (Fig. 1). Spectroscopic-grade graphite rods (6.4-mm diameter; National Carbon) were impregnated for 4 h by immersion in hot ceresin wax

(Fisher) under vacuum. Previous work [14] suggested relatively low residual currents for this wax type in addition to other desirable properties [15]. Graphite electrode components were machined with a small lathe (Unimat, American Edelstaal Corp.). A thin layer of graphite was removed with a microtome blade to produce a homogeneous surface of approximately 300 mm^2. Components were force fitted into Teflon (FEP) tubing. The electrode was used indefinitely with the aid of the surface-conditioning process described below.

Each time the electrode was prepared for mercury plating, a final surface preparation was made by first wiping the surface clean with a soft tissue, immersing the machined graphite surface in hot ceresin wax (5 min), and then allowing a uniform coating to harden completely on it. While the electrode was rotated in the lathe at moderate speed, several clean surfaces of a relatively hard bond typing paper were used to rub off the wax by applying firm finger pressure. This process also removed a thin layer of graphite to form a new surface onto which the mercury was plated.

To form the mercury film, the electrode was rinsed with deionized distilled water and placed in the a.s.v. cell containing 10 ml of previously degassed mercury(II) nitrate solution (200 mg l^{-1}) which was 0.1 M in nitric acid. The solution was degassed for an additional 1 min, and allowed to become quiescent before −0.8 V (vs. Ag/AgCl, 0.1 M (NaCl)) was applied to the working electrode for 3 min. The electrode was immediately removed from the solution and rinsed. The total amount of mercury which could be electrochemically stripped from the electrode was approximately 0.1—0.3 μg mm^2 (calculated area) as determined by a standard cold-vapor mercury atomic absorption procedure [16]. A solution containing 10 μg Cd l^{-1}, 10 μg Pb l^{-1}, 10 μg Cu l^{-1}, 5 mg Hg l^{-1} and 0.2% (v/v) nitric acid was then analyzed repeatedly with a 1-min plating time at −1.2 V and a linear sweep of 5 V min^{-1} to test whether acceptable response was obtained. A properly prepared electrode gave reproducible (±2%) sharp peaks with half-peak widths of about 0.04 V and peak currents in the range of 10 μA. The background current was approximately 1—2 μA and the hydrogen overvoltage was −1.2 V. The time required from the wax surface conditioning step to this point was about 30 min.

Apparatus

Data were recorded on a Hewlett-Packard Model 2D-2 X-Y recorder. A modified [17] polarographic module (Heathkit, Model EUA-19-2) was used for applying plating potentials and linear d.c. voltage sweeps. Control functions on the module were particularly suited for nulling out the background current from the electrode so that a high current sensitivity could be achieved. The design of the cell assembly was similar to one described previously [11] with a few exceptions. Main component parts were a 78 × 22-mm diameter (i.d.) flat-bottom fused quartz cell (General Electric, Willoughby, Ohio) convenient for 10-ml samples, a machined Teflon cell

head, an auxiliary electrode, and a Ag/AgCl (0.1 M NaCl) reference electrode. The auxiliary electrode consisted of a platinum wire (6 cm long by 0.5 mm in diameter) in a 3-mm i.d. FEP tube filled with 0.1 M NaCl and stoppered at the bottom with a leached porous quartz plug (Corning Glass Works, Danville, Virginia). The reference electrode was a silver chloride-coated wire, which was also immersed in 0.1 M NaCl contained in a Teflon tube with a porous quartz stopper. FEP capillary tubing (0.5-mm i.d.), with a platinum wire placed inside for stiffening, was used for dispersing water-saturated, prepurified-grade nitrogen through the cell solution to expel oxygen. A 3 × 14-mm Teflon-encapsulated magnetic stirring bar (1000 rpm) was also used to stir the solution during the plating step.

Reagents

All chemicals were of analytical-reagent grade, but ultrapure nitric acid (Baker Ultrex) was generally used for lead determinations. Ultrapure water was prepared by passing distilled water through a deionizer (Millipore Super Q). Standards were prepared by weighing and dissolving the required amount of pure metal in nitric acid and making appropriate dilutions with 0.2% (v/v) nitric acid.

Procedure

Quartz cells were cleaned and kept separate for the analysis of samples of low concentration. The cleaned cell was immediately checked for contamination by analyzing a 10-ml aliquot of acidified deionized distilled water. The acidified (0.2% v/v HNO_3) sample or blank was degassed for 2 min and stirred, after which a plating potential of −1.2 V for cadmium and lead, or −1.0 V for lead and copper, was applied for 1−5 min. Stirring was then ceased and the solution was allowed to become quiescent for 30 s, thus allowing time for the background current to decay to a minimum before balancing it to near zero. The voltage was swept from −1.0 to 0.0 V at 5−10 V min^{-1}. Application of potentials near or more positive than 0.0 V was avoided since this reduces the normal useful lifetime of the mercury film. Each sample was analyzed in duplicate; two or more different standard concentrations were then added for calibration by the method of standard additions.

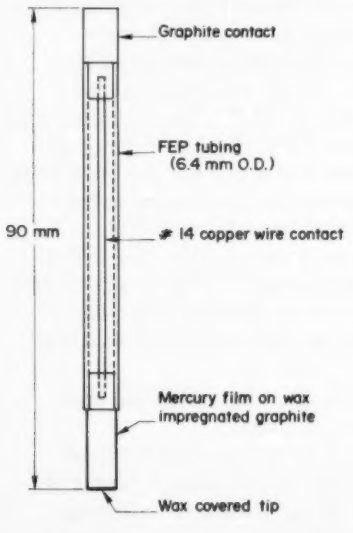
Aspects of furnace atomic absorption analysis (f.a.a.s.), sampling and sample preparation have been discussed previously [18].

Samples were digested by dispensing 15-ml aliquots into a precleaned Teflon-lined pressure decomposition bomb (Parr). In addition, 0.15 ml of 10% (w/w) ammonium persulfate (Baker) was added if greater oxidizing conditions were desired. The bomb was hand-tightened and then turned an additional one-quarter turn before it was placed in an oven for 3 h at 140°C. Water samples originally high in natural color because of humic materials appeared colorless after digestion. Blanks were run and standards were

periodically added to the digestion vessel to check on recoveries. Sample cups were cleaned between digestions with ultrapure (1 + 1) nitric acid, followed by 0.2% (v/v) nitric acid, as employed in the normal digestion procedure.

RESULTS AND DISCUSSION

A.s.v. with a hanging mercury drop or mercury film electrode has been widely studied [19—22]. Although the performance of each system is a function of the type of electrode and the electronics, one limiting property of wax-impregnated graphite mercury film electrodes has been that they have finite lifetimes which are an integrated function of electrode substrate, mercury film characteristics, the chemical characteristics of the samples with which they come in contact, and the voltage ranges in which they are used. Since it is commonly necessary for the analyst routinely to prepare the surface of film electrodes, it was desirable to produce a sensitive electrode that could be prepared rapidly and reproducibly, i.e. the time involved should be several minutes rather than several hours. Such an electrode is described above. About 30 min was required for the surface-conditioning step and mercury plating. This relatively rapid procedure helped to circumvent the problems of analyzing acidified samples, since electrode lifetime was often shorter at low pH. Oxidation of active sites on the graphite



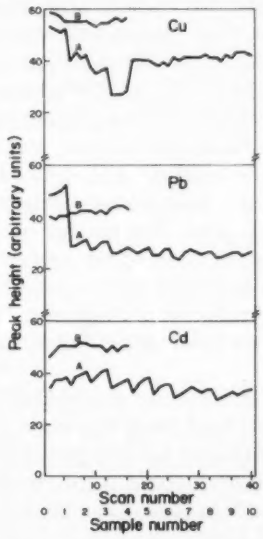


Fig. 1. Construction of wax-impregnated mercury film graphite electrode.

Fig. 2. Variations in peak height as a function of repeatedly analyzing a Lake Superior water sample containing added metal ions. Curve A represents quadruplicate scans on each of ten cell solutions; Curve B indicates several scans on the same cell solution.

surface can occur more easily as the pH decreases [23]. This condition gives rise to larger background currents and a more positive overvoltage, which can make an electrode less useful. However, this problem was offset by employing an in situ mercury plating procedure with solutions containing usually 2 mg $Hg\,l^{-1}$. The sensitivity of the electrode appeared to be relatively stable once a sufficient mercury film had been formed [6]. Peak current was a linear function of scan rate in the range 1—10 V min^{-1}.

Typical changes in electrode sensitivity were characterized as a function of electrode use by repeatedly analyzing a metal-spiked Lake Superior water sample containing 1—2 $\mu g\,l^{-1}$ each of cadmium, lead and copper (Fig. 2). The experiment was treated as routinely as possible; therefore, no special care was taken other than in normal analytical procedures. A new electrode surface was prepared just prior to each series of analyses (A and B). In curve A each sample-analysis sequence consisted of four scans on the same cell solution containing 2 mg l^{-1} mercury(II) with 2-min plating times. After each sequence the cell solution was replaced with an aliquot of the same sample for a total of 10 times, which produced 40 scans on a single acidified (0.2% v/v HNO_3) water sample. Most apparent is the relatively good reproducibility in all cases for quadruplicate scans on a single cell solution, although a noticeable upward trend of peak current with each successive scan is apparent in some groups. At the beginning of Curve A, marked differences are noted between the means of quadruplicates for copper and lead on different cell solutions of the same sample. These differences may be partly due to contamination or adsorption effects; however, past experience suggests that this is not the reason since the slope of the standard additions curve can also change between different cell solutions. For cadmium these changes are not quite so pronounced but are still apparent. Therefore, these data suggest that in sample analysis standard additions should be used to obtain the best calibration. In illustration of this point, analysis of a Lake Superior sample in triplicate for cadmium and lead at their ambient concentrations gave values of 0.023, 0.023 and 0.024 $\mu g\,l^{-1}$ for cadmium and 0.15, 0.17 and 0.18 $\mu g\,l^{-1}$ for lead. Each replicate represented separate cell solutions with duplicate scans of the cell solution and two additional scans with standard addition spikes. Curve B, representing several repeated scans on the same cell solution, shows excellent reproducibility. Figure 3 illustrates the linear nature of a typical standard addition graph for the determination of cadmium in Lake Superior water.

A display of experimental output is given in Fig. 4 with duplicate determinations of cadmium and lead in natural water giving mean concentrations of 0.055 $\mu g\,l^{-1}$ and 0.28 $\mu g\,l^{-1}$ respectively. Natural fresh-water concentrations for copper are usually in a much higher range; these determinations were done separately giving a mean copper value of 0.45 $\mu g\,l^{-1}$. Higher sensitivity can normally be obtained by increasing plating time and scan rate.

Contamination from the cell and acid was a major concern in routinely determining baseline samples. It was highly desirable to clean the cell thoroughly

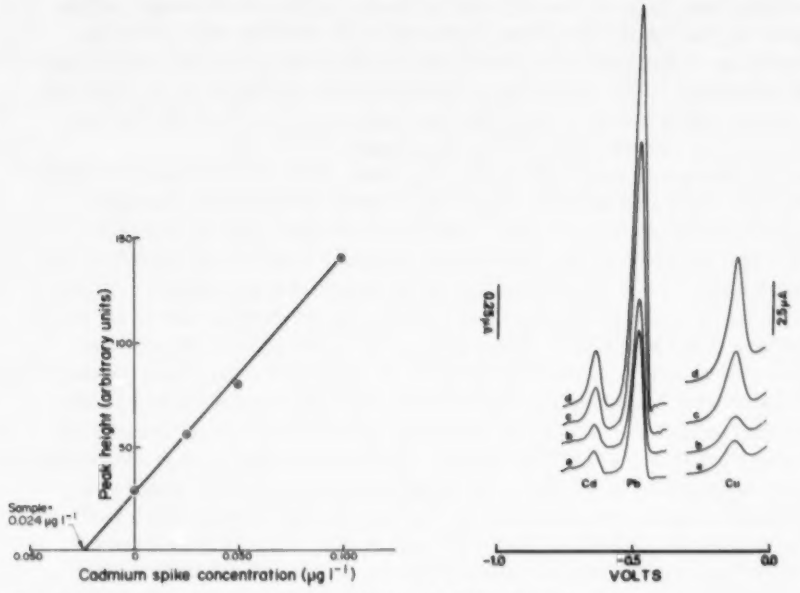


Fig. 3. Standard addition plot for cadmium in Lake Superior water.

Fig. 4. A.s.v. analysis of a natural water sample. Scan rate, 5 V min^{-1}; plating time, 90 s. Curves a and b, sample. Curve c, sample + 0.05 μg Cd l^{-1} + 0.25 μg Pb l^{-1} + 1 μg Cu l^{-1}. Curve d, sample + 0.1 μg Cd l^{-1} + 0.5 μg Pb l^{-1} + 2 μg Cu l^{-1}. Results: Cd, 0.055 μg l^{-1}; Pb, 0.28 μg l^{-1}; Cu, 0.45 μg l^{-1}.

TABLE 1

Typical analysis blanks[a]

Element	Mean concentration (μg l^{-1})	Standard deviation (μg l^{-1})	Number
Cd	<0.005	—	9
Pb	0.017	0.008	9
Cu	<0.03	—	4

[a]0.2% (v/v) nitric acid (Baker Ultrex) in deionized distilled water.

and analyze a cell blank (0.2% v/v HNO_3), particularly for cadmium and lead. Table 1 gives typical minimum blank values that could be routinely attained. Lead contamination was the most troublesome, which is reflected in a somewhat variable mean blank value of 0.017 μg l^{-1}. This concentration could easily be detected since the instrumental detection system was sensitive

TABLE 2

Typical reproducibilities and detection limits for the analysis of natural water samples

Element	Mean relative error[a] (%)	Range (%)	No. of determinations	Estimated working detection limit ($\mu g\ l^{-1}$)
Cd	11.6	2.1—32.8	24	0.005[b] (0.005)[d]
Pb	7.4	0.5—26.6	54	0.03[c] (0.005)[d]
Cu	4.3	0.2—15.1	45	0.03[b] (0.03)[d]

[a]Defined as the mean of the relative deviation from the mean for two analyses on each of several water samples. Concentration ranges: Cd, 0.005—0.28 $\mu g\ l^{-1}$; Pb, 0.06—3.2 $\mu g\ l^{-1}$; Cu, 0.5—7.7 $\mu g\ l^{-1}$.
[b]Estimated working detection limit defined as twice the mean of the deviation from the mean for two analyses on each of several water samples with very low concentrations. Cd < 0.03 $\mu g\ l^{-1}$ and Cu < 1.0 $\mu g\ l^{-1}$.
[c]Estimated working detection limit based on the cell blank plus twice its standard deviation.
[d]Estimated instrumental detection limit for a 5-min plating time.

to about 0.005 $\mu g\ l^{-1}$. Therefore, measurement of these baseline samples was largely dependent on maintaining the blank in this low range.

Since normal analytical procedure involved two analyses of a sample prior to spiking, their repeatability was a measure of the precision for a single analysis of a sample. Table 2 gives values for this reproducibility involving 24—45 analyses on different natural water samples. Concentrations covered a wide range for all three metals, but the mean concentrations were low (0.03 μg Cd l^{-1}, 0.03 μg Pb l^{-1}, 2 μg Cu l^{-1}). Mean relative errors ranged from 11.6% for cadmium to 4.3% for copper, which are acceptable. The estimated working detection limit for lead was calculated from the blank plus twice its standard deviation. For cadmium and copper, it was based on twice the mean of the deviation from the mean for duplicate determinations on each of several water samples containing very low concentrations. Concentrations were limited to $\leq 0.03\ \mu g\ l^{-1}$ for cadmium and $\leq 1.0\ \mu g\ l^{-1}$ for copper in this calculation. Estimated instrumental detection limits (not considering the reagent blank) were based on a concentration corresponding to a peak height deflection double the width of the baseline noise, with maximum scale expansion and a 5-min plating time. All values are acceptable for the analysis of natural waters and compare favorably with values obtained by other methods [6—13].

It is generally accepted that samples often require digestion if the total metal concentration (rather than "acid exchangeable metal") is the desired parameter. However, the digestion step introduces an additional possibility for contamination. In view of this, a relatively new digestion technique was explored: digestion at 140°C for 3 h in a Teflon-lined pressure decomposition

bomb. This method possesses the inherent advantages of a completely closed system to avoid the possibility of contamination via air during digestion and a higher digestion temperature without taking a sample to incipient dryness. Persulfate may also be added to increase oxidizing conditions. However, even without added persulfate, natural water samples, normally colored because of naturally occurring organic matter, were essentially decolorized. Ultraviolet spectrophotometric absorbance measurements on digested samples indicated a five to tenfold decrease in absorbance compared to the undigested sample, which was assumed to be due to decomposition of organic matter.

The results of a.s.v. measurements on undigested samples (samples 1—15), digested samples without added persulfate (samples (9—15) and digested samples with added persulfate (samples 9—15) are given in Table 3. All were natural water samples from wilderness streams in north-eastern Minnesota and from Lakes Superior and Huron and their tributary streams. For lead, there is a good correspondence between acid-exchangeable values and those corresponding to digested samples (total values), even with persulfate added. For copper, however, markedly lower values were obtained for acid-exchangeable metal compared to either digested or persulfate-digested samples. In some cases, the acid-exchangeable result was only one-half the total concentration. Little or no difference was observed with or without the presence of persulfate in the digestion. Filtered (0.1 μm) samples exhibited the same differences between undigested and digested samples. Therefore, it is likely that differences should be attributed not to dissolution of suspended solids, but to release of copper from electro-inactive dissolved complexes or colloidal forms which are slow to dissociate (since samples remained acidified for at least 1 week before measurement).

Because of these results, it was especially desirable to determine the possible accuracy of a.s.v. determinations by making comparative analyses with f.a.a.s. (Table 3). For the f.a.a.s. measurement, simultaneous deuterium arc background correction was always employed and calibration was by the method of standard additions. Results for copper analyses (samples 9—15) show a high degree of correlation between a.s.v. for digested samples and f.a.a.s. for either digested or undigested samples, which demonstrates the validity of the digestion step for the a.s.v. analyses. The f.a.a.s. results for lead (either undigested or digested samples) generally agree well with a.s.v. results on digested or undigested samples (acid exchangeable). Also given in Table 3 are the results of several analyses for total cadmium by f.a.a.s. and acid-exchangeable cadmium by a.s.v. The close agreement for most samples suggests that acid-exchangeable cadmium is essentially equal to the total cadmium in these cases. However, it is possible that sample digestion may be required for the determination of total cadmium for other natural waters.

Results of a.s.v. analyses for a survey of relatively unpolluted baseline natural waters of low turbidity are given in Table 4. All values correspond to acid-exchangeable metals in unfiltered samples. Over a period of several months, surface-water samples from streams in a wilderness area of north-

TABLE 3

Relationship of sample digestion to a comparison of analytical results for natural waters by a.s.v. and f.a.a.s.

Sample	Sample type[a]	Copper ($\mu g\ l^{-1}$)		Lead ($\mu g\ l^{-1}$)		Cadmium ($\mu g\ l^{-1}$)	
		F.a.a.s.[b]	A.s.v.	F.a.a.s.	A.s.v.	F.a.a.s.	A.s.v.
1[c]	UF, UD	—	—	0.2	0.20	0.031	0.013
2[c]	UF, UD	—	—	0.3	0.17	0.021	0.013
3[c]	UF, UD	—	—	0.3	0.21	0.022	0.021
4[c]	UF, UD	—	—	0.5	0.30	0.034	0.022
5	UF, UD	—	—	0.2	0.17	0.020	0.022
6	UF, UD	—	—	1.0	0.93	0.27	0.28
7	UF, UD	3.3	2.8	0.8	0.92	0.26	0.29
8	UF, UD	1.7	1.4	0.2	0.34	0.070	0.076
9	UF, UD	1.1	0.51	0.2	0.18	—	—
	UF, D	1.0	0.80	0.2	0.18	—	—
	UF, DP	—	0.99	—	0.19	—	—
10[c]	UF, UD	6.2	3.2	0.4	0.10	0.019	0.034
	UF, D	5.6	6.0	—	—	—	—
11	UF, UD	1.2	0.85	0.4	0.23	0.032	0.030
	UF, D	1.0	0.90	—	—	—	—
12[c]	F, UD	5.6	3.0	—	—	—	—
	F, D	6.3	6.5	—	—	—	—
13	F, UD	1.6	0.65	0.3	0.26	0.29	0.23
	F, D	1.4	1.5	0.3	0.23	—	—
	F, DP	—	1.3	—	0.30	—	—
14[c]	F, UD	2.4	1.3	0.4	0.39	0.13	0.16
	F, D	2.2	2.0	0.4	0.42	—	—
	F, DP	—	1.7	—	0.34	—	—
15	F, UD	1.6	0.70	0.2	0.09	0.10	0.043
	F, D	1.5	1.2	0.2	0.10	—	—

[a]UF = unfiltered acidified, F = filtered (0.1 μm) acidified, UD = undigested, D = pressure-digested, DP = pressure-digested with 0.1% (w/w) ammonium persulfate.
[b]Working f.a.a.s. detection limits: Cu = 0.2, Pb = 0.2, Cd = 0.008 $\mu g\ l^{-1}$.
[c]Indicates colored sample containing natural organic material; all other samples were low in color. All samples were of low turbidity.

TABLE 4

Analysis by a.s.v. of selected baseline natural waters[a]

Element	Mean concentration[b] ($\mu g\ l^{-1}$)	Standard deviation ($\mu g\ l^{-1}$)	Range ($\mu g\ l^{-1}$)	No. of determinations
Cd	0.019	0.008	0.006—0.034	18
Pb	0.18	0.051	0.10—0.30	27
Cu	1.25	1.09	0.46—3.35	10

[a]From western Lake Superior, at the Environmental Research Laboratory-Duluth, Duluth, Mn. and streams of Superior National Forest located in wilderness areas of north eastern Minnesota [18].
[b]Corresponds to acid-exchangeable metal for unfiltered acidified samples.

eastern Minnesota were collected directly into precleaned polyethylene or FEP containers and acidified to 0.2% (v/v) nitric acid. Lake Superior samples were also collected at the Environmental Research Laboratory in Duluth, Minnesota. Large concentration differences were not discerned with respect to time or location; concentrations were very similar at all stations (with the exception of copper for one stream in which the value was 3.4 $\mu g\ l^{-1}$). Mean values generally compared favorably with studies [10, 24] for other areas.

REFERENCES

1 U.S.—Canadian International Joint Commission, Upper Lakes Reference Group Report, The Waters of Lake Huron and Lake Superior, 1977, Vols. II, III.
2 K. E. Biesinger and G. M. Christensen, J. Fish. Res. Board Can., 29 (1972) 1691.
3 J. M. McKim and D. A. Benoit, J. Fish. Res. Board Can., 28 (1971) 655.
4 G. W. Holcombe, D. A. Benoit, E. N. Leonard and J. M. McKim, J. Fish. Res. Board Can., 33 (1976) 1731.
5 D. A. Benoit, E. N. Leonard, G. M. Christensen and J. T. Fiandt, Trans. Am. Fish. Soc., 4 (1976) 550.
6 M. Branica, L. Sipos, S. Bubic and S. Kozar, Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis, Vol. II, U.S. National Bureau of Standards Special Publication #422, Proceedings of the 7th IMR Symposium, October 1974, Gaithersburg, Md., 1976, p. 917.
7 D. Jagner and L. Kryger, Anal. Chim. Acta, 80 (1975) 255.
8 W. Lund and M. Salberg, Anal. Chim. Acta, 80 (1975) 131.
9 A. H. Miguel and C. M. Jankowski, Anal. Chem., 46 (1974) 1832.
10 H. W. Nürnberg, P. Valenta, L. Mort, B. Raspor and L. Sipos, Fresenius Z. Anal. Chem., 282 (1976) 357.
11 H. E. Allen, W. R. Matson and K. H. Mancy, J. Water Pollut. Control Fed., 42 (1970) 573.
12 T. R. Copeland, J. H. Christie, R. A. Osteryoung and R. K. Skogerboe, Anal. Chem., 45 (1973) 2171.
13 M. I. Abdullah, B. Reusch Berg and R. Klimek, Anal. Chim. Acta, 84 (1976) 307.
14 V. F. Gaylor, A. L. Conrad and J. H. Landerl, Anal. Chem., 29 (1957) 224.
15 R. G. Clem and A. F. Sciamanna, Anal. Chem., 47 (1975) 276.
16 G. F. Olson, D. I. Mount, V. M. Snarski and T. W. Thorslund, Bull. Environ. Contam. Toxicol., 14 (1975) 129.
17 R. W. Andrew, Chem. Instrum., 6 (1975) 163.
18 J. E. Poldoski and G. E. Glass, Proceedings of the International Conference on Heavy Metals in the Environment, Vol. II, October, 1975, Toronto, Ontario, Canada, 1977, p. 901.
19 R. A. Osteryoung and J. H. Christie, Anal. Chem., 46 (1974) 351.
20 W. T. DeVries and E. Van Dalen, J. Electroanal. Chem., 14 (1967) 315.
21 W. R. Matson, D. K. Roe and D. E. Carritt, Anal. Chem., 37 (1965) 1594.
22 T. M. Florence, J. Electroanal. Chem., 27 (1970) 273.
23 R. G. Clem, Anal. Chem., 47 (1975) 1778.
24 J. Kubota, E. L. Mills and R. T. Oglesby, Environ. Sci. Technol., 8 (1974) 342.